2034

MTL TR 86-4

AD A167559

A167559

SERIAL CHROMATOPYROGRAPHY-MASS SPECTROMETRY OF NATURAL RUBBER VULCANIZATES

ALFRED J. DEOME and CHRISTOPHER J. KULIG
POLYMER RESEARCH DIVISION

JACOB PATT
U.S. ARMY TANK-AUTOMOTIVE COMMAND

March 1986

Approved for public release; distribution unlimited.

20020806121

Sponsored by
U.S. ARMY TANK-AUTOMOTIVE COMMAND
Warren, Michigan 48090

US ARMY
LABORATORY COMMAND
MATERIALS TECHNOLOGY
LABORATORY

U.S. ARMY MATERIALS TECHNOLOGY LABORATORY
Watertown, Massachusetts 02172-0001

AW-23313

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER MTL TR 86-4	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) SERIAL CHROMATOPYROGRAPHY-MASS SPECTROMETRY OF NATURAL RUBBER VULCANIZATES		5. TYPE OF REPORT & PERIOD COVERED Final Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Alfred J. Deome, Christopher J. Kulig, and Jacob Patt*		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Army Materials Technology Laboratory Watertown, Massachusetts 02172-0001 ATTN: SLCMT-OP		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS D/A Project: 1L162601AH91
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Tank-Automotive Command Warren, Michigan 48090		12. REPORT DATE March 1986
		13. NUMBER OF PAGES 20
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

*U.S. Army Tank-Automotive Command, Warren, MI 48090

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Gas chromatography	Pyrolysis
Mass spectrometry	Natural rubber

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

SEE REVERSE

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Block No. 20

ABSTRACT

Applications of serial pyrolysis-gas chromatography-mass spectrometry, developed at the U.S. Army Materials Technology Laboratory, are used to determine the qualitative organic formulation and polymer composition of two proprietary experimental natural rubber formulations.

INTRODUCTION

Previous work in the area of pyrolysis-gas chromatography-mass spectrometry[1-5] has shown that this technique is a powerful analytical tool well suited for studying the complex composition of intractable materials, such as vulcanized elastomers. An interesting and particularly valuable application of the many pyrolysis techniques available is serial chromatopyrography-mass spectrometry (Ser-Py-GC-MS). This technique appears to be very applicable to separating residual vulcanizate formulation components from polymer composition without the need for complicated sample manipulation procedures. Instrumental techniques employing a combination of serial pyrolysis techniques, high resolution capillary gas chromatography, and mass spectrometry have been developed at the U.S. Army Materials Technology Laboratory, Watertown, MA, in collaboration with the U.S. Tank-Automotive Command (TACOM), Warren, MI, during the last several years. The technique is used as a means of accurately accessing and reconstructing formulations of vulcanized elastomers where few, if any, straightforward analytical procedures are available for this type of work.

This report documents the application of Ser-Py-GC-MS in determining the composition of two experimental natural rubber formulations. The vulcanized tensile sheets, both of proprietary composition, are referenced in this report as Sample LG-1 (465 VI and II) and Sample LG-2 (465 X-5).

EXPERIMENTAL

Thermal gravimetric analysis (TGA) was performed on each sample using a DuPont 1090 thermal analyzer to determine temperature profiles at which the organic formulation is thermally desorbed from the polymer and inorganic component matrix of the vulcanizates. Pyrolysis experiments were performed on each sample using a Chemical Data Systems, Inc., Model 122 pyrolysis unit interfaced to a Hewlett-Packard Model 5996 gas chromatograph-mass spectrometer system under computer control (Hewlett-Packard 1000 Data System). The samples were each subjected to an initial pyrolysis temperature of 350°C followed serially by a second pyrolysis at 600°C. The pyrolyzate from each experiment was chromatographed on a 12-meter fused silica capillary column of crosslinked methyl silicone (SE 30). The gas chromatograph was programmed from 50°C for 4 minutes to 280°C for 15 minutes at 10°C/minute. Mass spectra of the chromatographic effluent were collected and stored; a mass range of 33 to 450 amu was repeatedly scanned at approximately 1.5-second intervals for the selected mass range. Reconstructed mass pyrograms and mass spectra were generated subsequent to each analysis from the stored data. Identifications were facilitated by the use of computer library search routines of the Wiley-NBS data base of reference mass spectra.

1. DEOME, ALFRED J., KANE, PETER J., and PATT, JACOB. *The Determination of Temperature-Dependent Degradation Mechanisms in Track Pad Elastomers by Pyrolysis-Gas Chromatography-Mass Spectroscopy.* U.S. Army Materials Technology Laboratory, AMMRC TR 82-53, October 1982.
2. DEOME, ALFRED J., and HAGNAUER, GARY L. *Pyrolysis-Gas Chromatography-Mass Spectroscopy of AE 502 Rubber Fuel Hoses.* U.S. Army Materials Technology Laboratory, AMMRC TR 81-12, March 1981.
3. WUEPPER, JOHN L. *Pyrolysis Gas Chromatographic-Mass Spectrometric Identification of Intractable Materials.* Anal. Chem., v. 51, no. 7, 1979, p. 997.
4. IGLAUER, N., and BENLEY, F. F. *Pyrolysis GLC for the Rapid Identification of Organic Polymers.* J. Chromatog. Sci., v. 12, 1974, p. 23.
5. CHIH-AN HU, J. *Pyrolysis-Gas Chromatography Analysis of Rubbers and Other High Polymers.* Anal. Chem., v. 49, no. 4, 1977, p. 537.

RESULTS AND DISCUSSION

The thermal gravimetric analyses of the respective samples under investigation are shown in Figures 1 and 2. Both rubber sytsems appear to be very similar thermally in that the organic additive portions of both vulcanizates are liberated at temperatures of less than 350°C. The temperature region where the formulation is desorbed from the polymer is critical in order to separate the additives from the polymer during the serial pyrolysis experiments. Table 1 shows the various temperature and weight loss relationships associated with the two samples under investigation.

Table 1. THERMAL GRAVIMETRIC ANALYSIS DATA

Sample	Organic Additives	Polymer	Filler	Residues
LG-1	361.0C (0.929 mg)	422.6C	618.6C	633.9C
LG-2	366.6C (1.00 6 mg)	428.5C	645.8C	660.9C

In order to desorb the organic formulation from the respective samples, a pyrolysis temperature of 350°C was selected. Samples weighing approximately 5 mg were used in the pyrolysis experiments. A quartz tube probe was heated at 20°C/ms and held at the maximum temperature for 20 seconds. The gas chromatograph program and data aquisition were then started. The 350°C mass chromatopyrograms of LG-1 and LG-2 are shown in Figures 3 and 4. These components represent the major portion of the formulation added to the rubber polymer during the mixing process. It would seem that the fatty acid materials of hexadecanoic and octadecanoic acids are derived from the polymer system rather than from the formulation. The antioxidant in both LG-1 and LG-2 is N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine; the mass spectrum of this component is shown in Figure 3a. Polymer identifications were achieved through pyrolysis of each sample at 600°C subsequent to each 350°C analysis. The reconstructed mass chromatopyrograms are shown in Figures 5 and 6. Essentially, these pyrograms indicate the presence of 2-methyl-1,3-butadiene (isoprene) as shown in Figure 5a.

In addition to the serial pyrolysis experiments performed, each sample was also extracted with acetone for 16 hours (ASTM D297). The extract was evaporated and concentrated to approximately 5 ml. Two microliters of each extract were injected using the gas chromatographic-mass spectrometric parameters previous described. The mass chromatograms are shown in Figures 7 and 8, respectively. The correlation of low temperature pyrolysis with the extract chromatography is excellent. The extract showed additional compounds indicative of the sulfur accelerator used in the formulation. The representative mass spectra corresponding to the individual components used for identification purposes are shown in Figures 7a, 7b, and 8a-8c.

CONCLUSIONS

Serial chromatopyrography-mass spectrometry experiments and gas chromatography-mass spectrometry of 16-hour acetone extracts have revealed a reasonably conclusive qualitative analysis of the formulation additives in Samples LG-1 and LG-2. The polymer is identified as cis-polyisoprene (natural rubber). The formulation additives are:

a. N-cyclohexyl-2-benzothiazole-2-sulfenamide (accelerator),

b. Hydrocarbon blend of wax or oil (processing/protective), and

c. N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (antioxidant).

Both samples are identical in qualitative formulation as evidenced from the results presented in this report. No attempt was made to evaluate these samples quantitatively. The polymer composition, shown to be of polymerized 2-methyl-1,3-butadiene (m/z 68) also shows various natural products and essential oils. There is no indication of polymer blending.

ACKNOWLEDGMENT

Appreciation is extended to Ms. Jane Brousseau for the thermal gravimetric analyses performed on these samples, and to Dr. Robert E. Sacher for his helpful interpretation of the data.

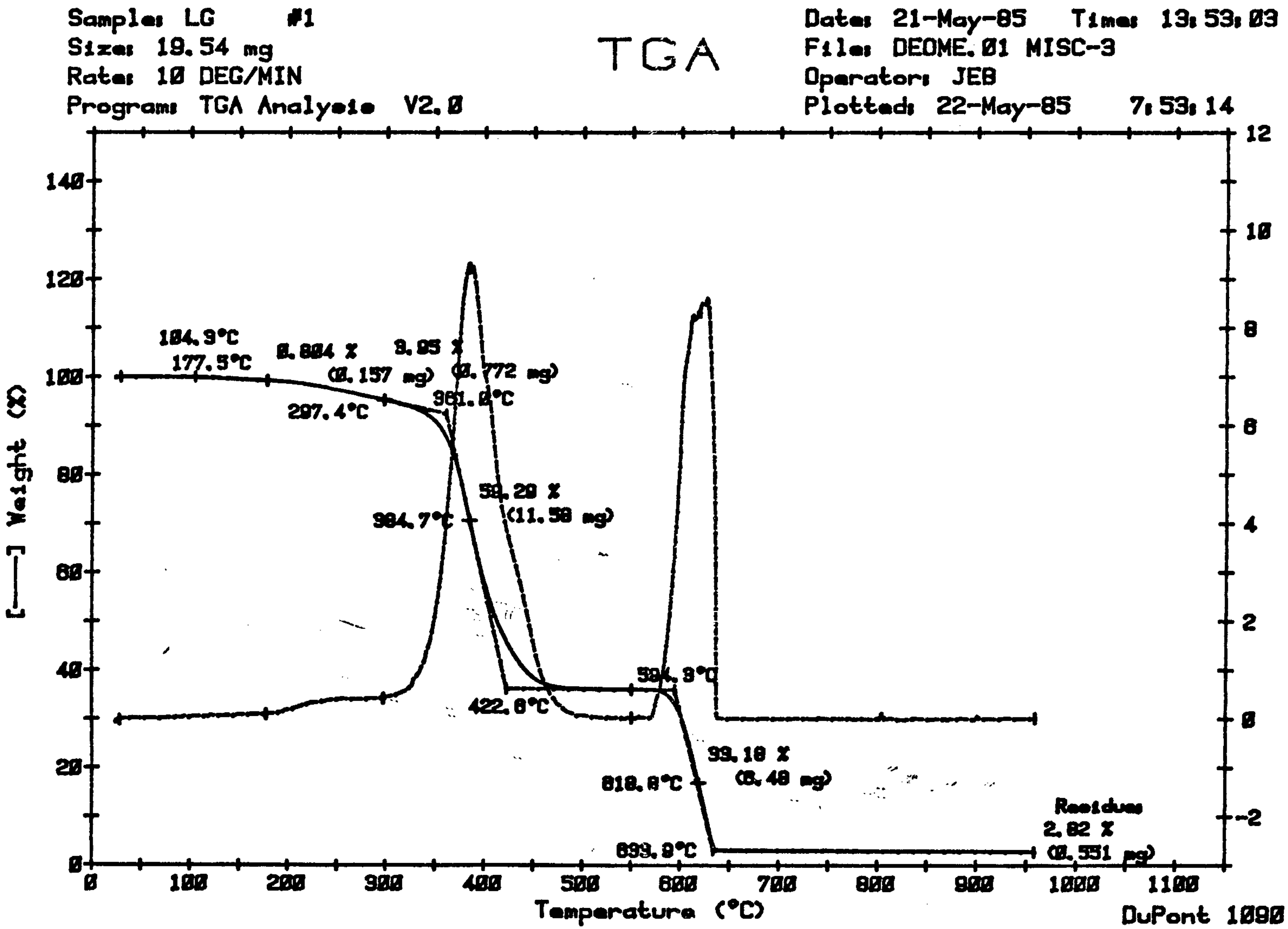


Figure 1. Thermal gravimetric analysis (TGA) of Sample LG-1.

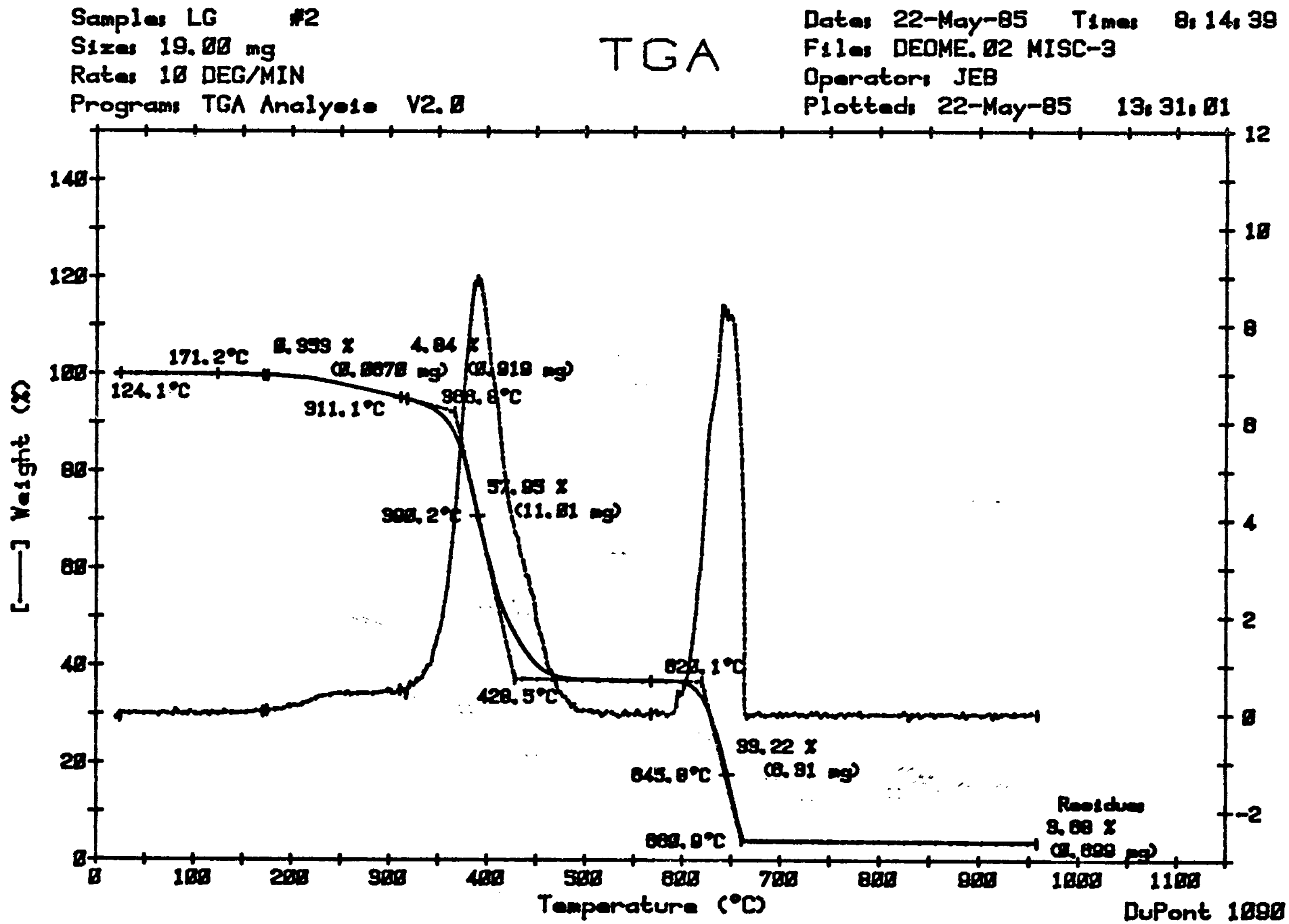
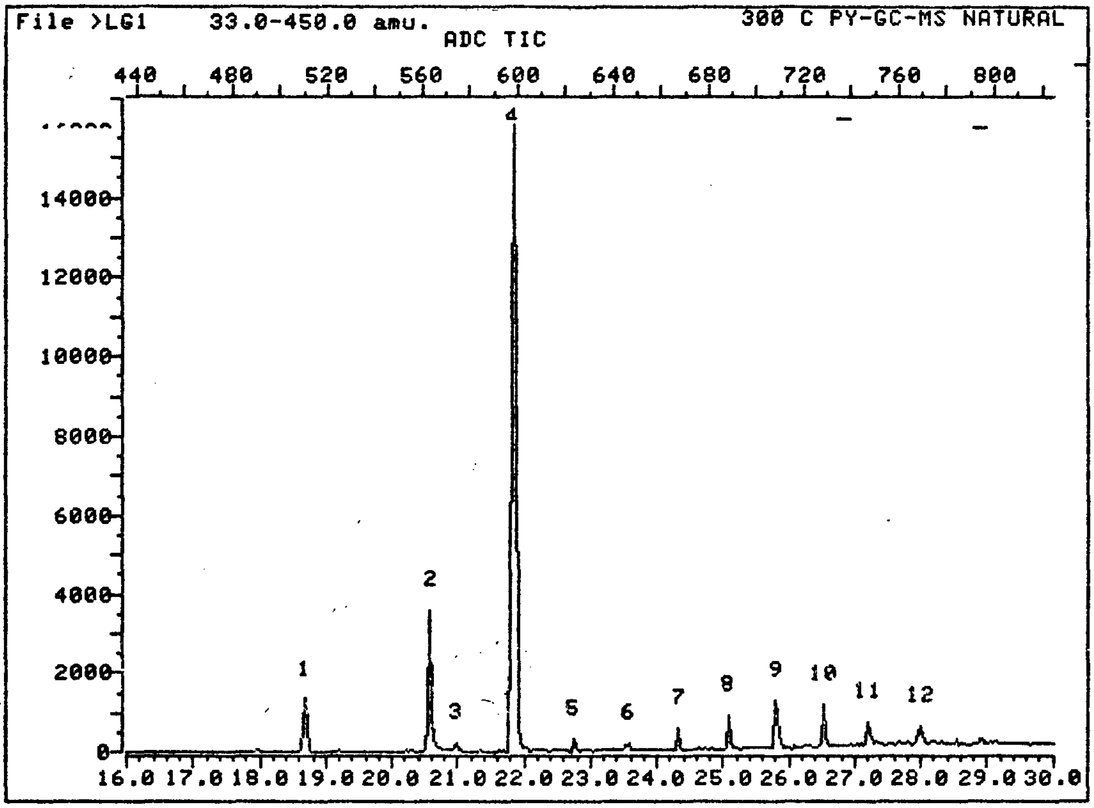


Figure 2. Thermal gravimetric analysis (TGA) of Sample LG-2.



COMPONENT IDENTIFICATION

1. Hexadecanoic Acid
2. Octadecanoic Acid (Stearic Acid)
4. N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (Antioxidant)
5 -12. Hydrocarbons

Figure 3. The reconstructed mass pyrogram of Sample LG-1 pyrolyzed at 350°C.

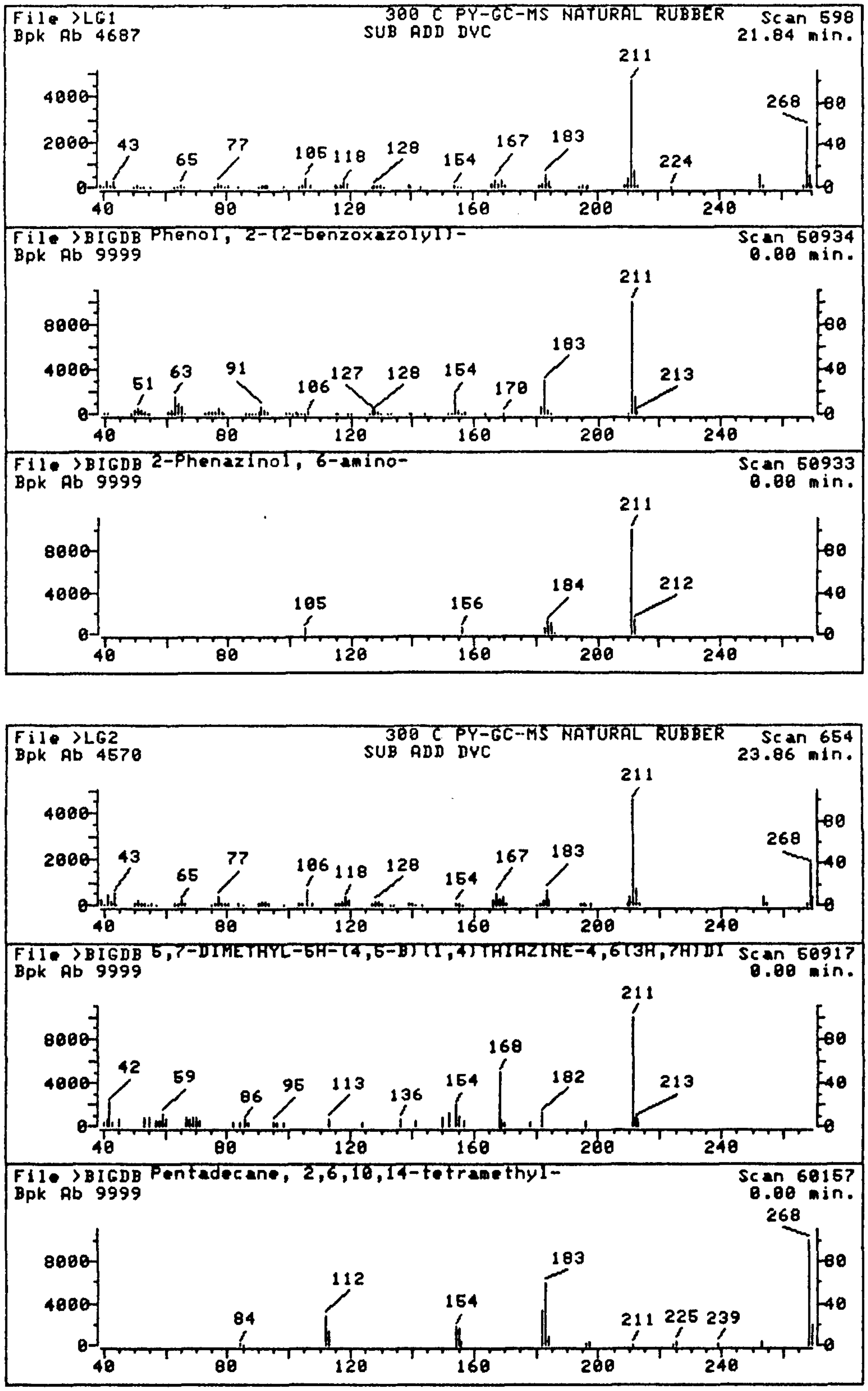
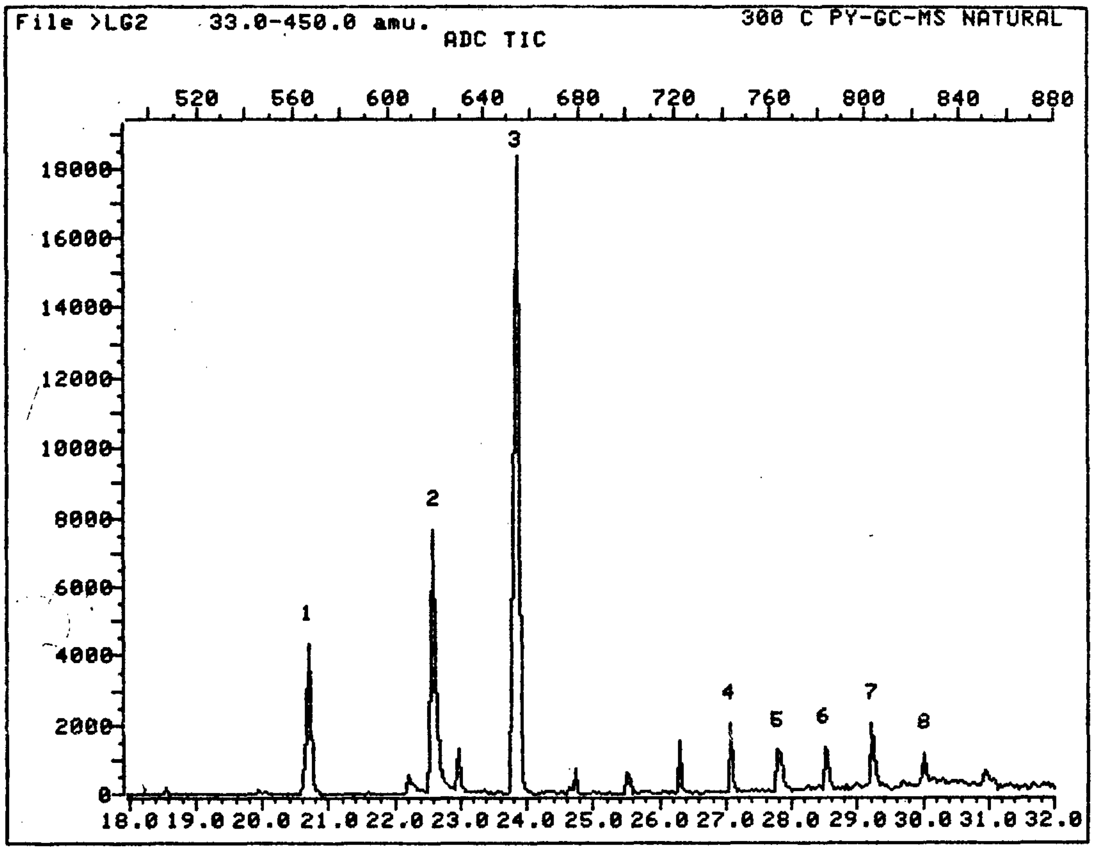


Figure 3a. The mass spectrum of the antioxidant [N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine], m/z 268, derived during the 350^{o}C pyrolysis experiments on LG-1 (top) and LG-2 (bottom).

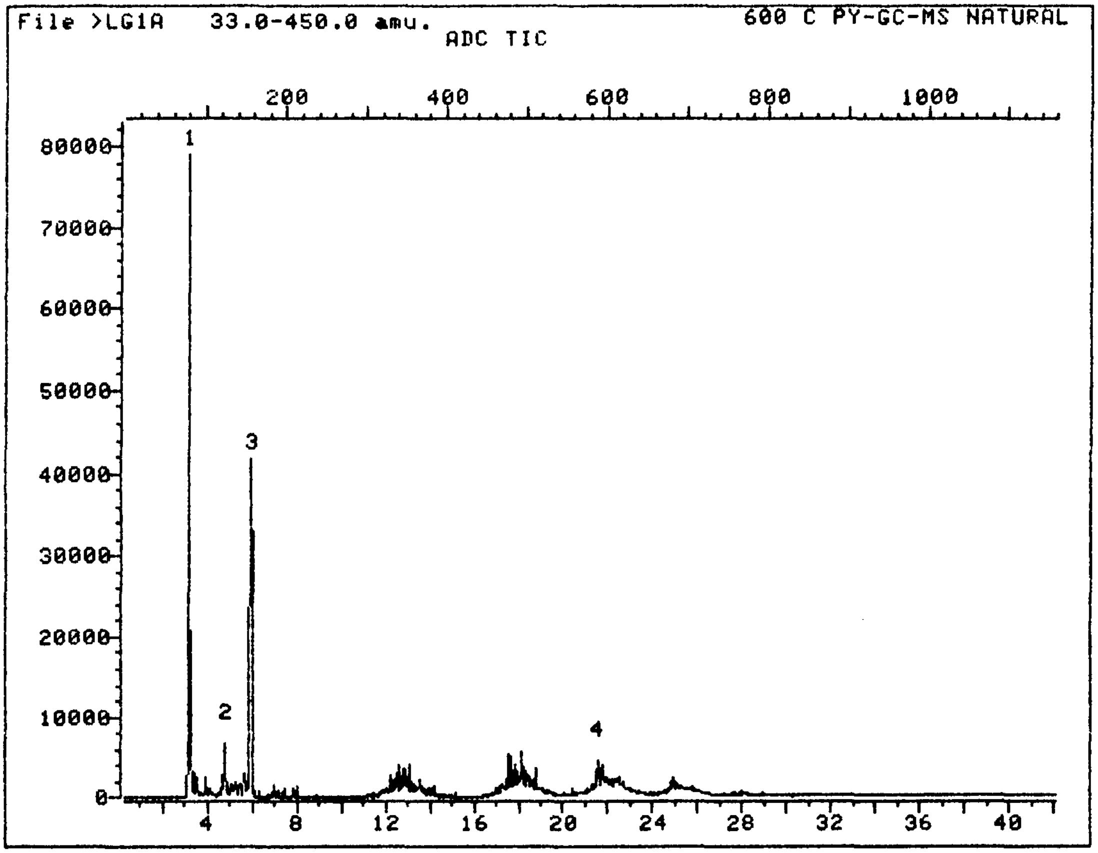


COMPONENT IDENTIFICATION

1. Hexadecanoic Acid
2. Octadecanoic Acid (Stearic Acid)
3. N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (Antioxidant)

4- 8. Hydrocarbons

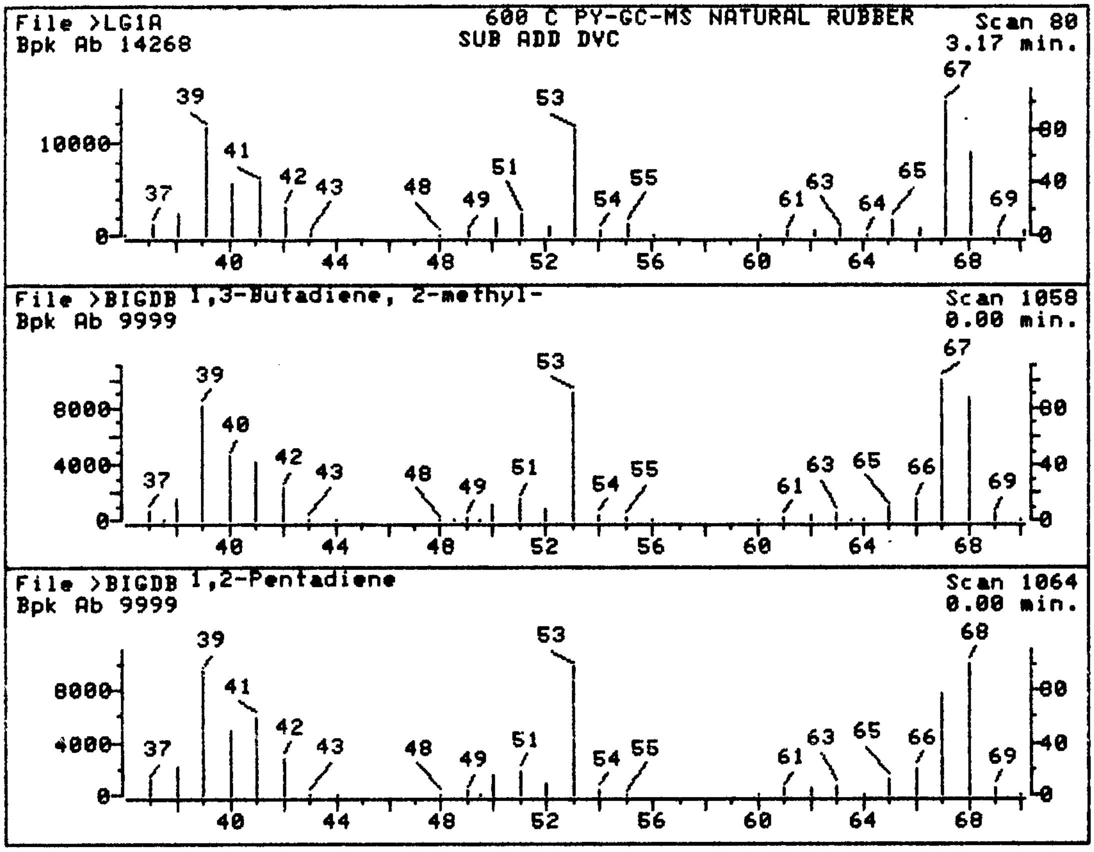
Figure 4. The reconstructed mass pyrogram of Sample LG-2 pyrolyzed at 350°C.



COMPONENT IDENTIFICATION

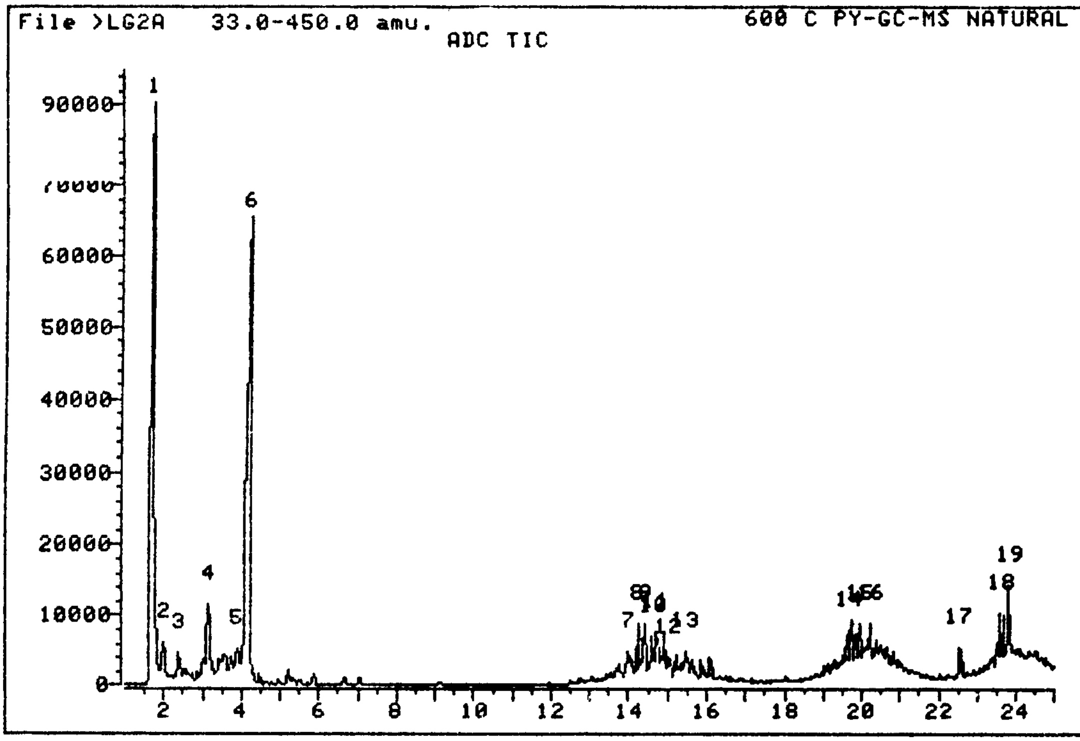
1. 2-Methyl-1,3-Butadiene (Isoprene)
2. Bornylene
3. Limonene
4. Natural Products

Figure 5. The reconstructed mass pyrogram of Sample LG-1 pyrolyzed at 600°C.



1. 1,3-Butadiene, 2-methyl- 68 C_5H_8
2. 1,2-Pentadiene 68 C_5H_8
3. 1,3-Pentadiene, (E)- 68 C_5H_8
4. 1,3-Pentadiene, (Z)- 68 C_5H_8
5. 1,3-Pentadiene, (Z)- 68 C_5H_8

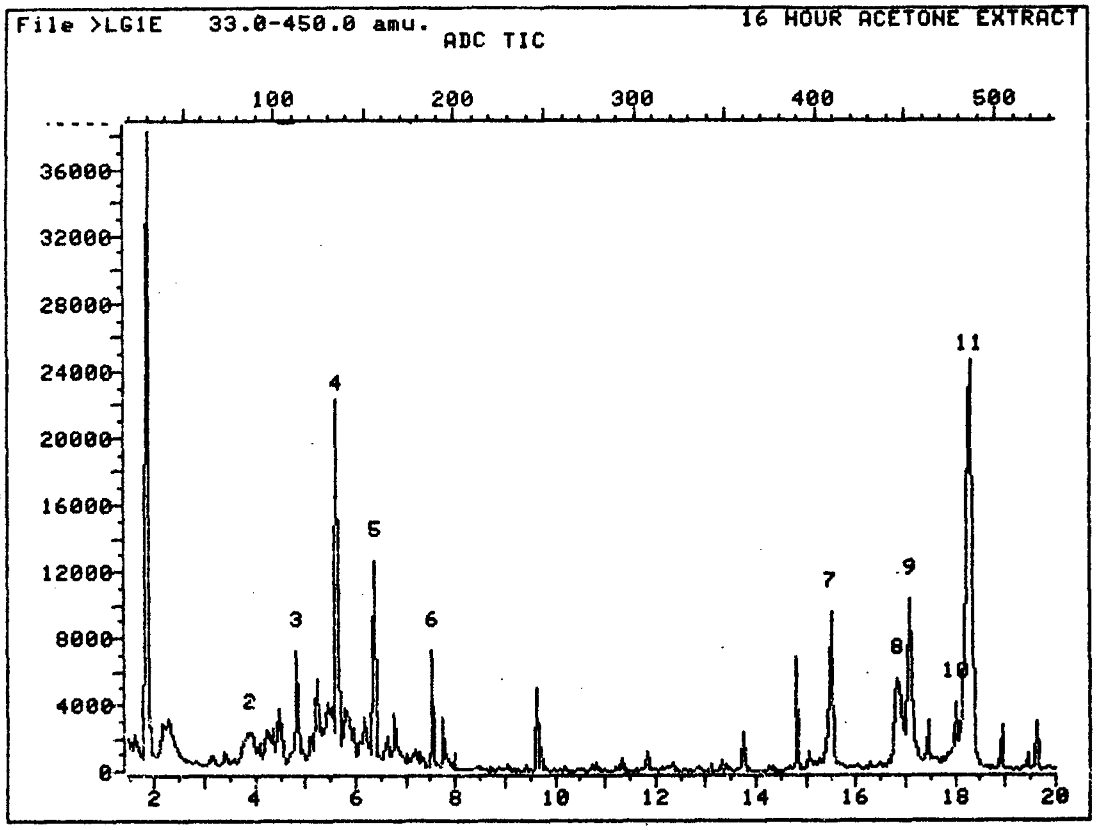
Figure 5a. The mass spectrum of isoprene (2-methyl-1,3-butadiene), m/z 68, resulting from the 600°C pyrolysis of Sample LG-1.



COMPONENT IDENTIFICATION

1. 2-Methyl-1,3-Butadiene (Isoprene)
2. 3-Methyl-1,3,5-Hexatriene
3. 1,4-Dimethylbenzene
4. 4-Vinyl-1,4-Dimethylcyclohexene
5. 2,7-dimethyl-3-octen-5-yne
6. Limonene
7. Farnesene

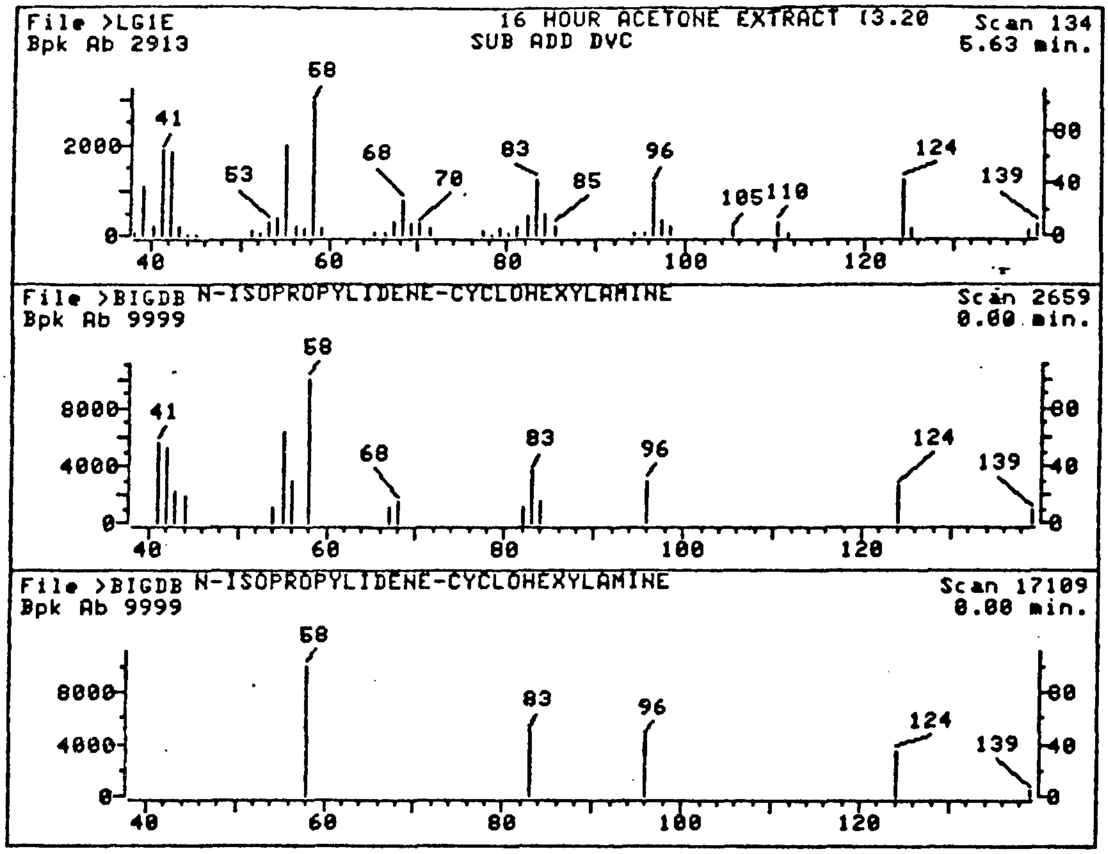
Figure 6. The reconstructed mass pyrogram of Sample LG-2 pyrolyzed at 600°C.



COMPONENT IDENTIFICATION

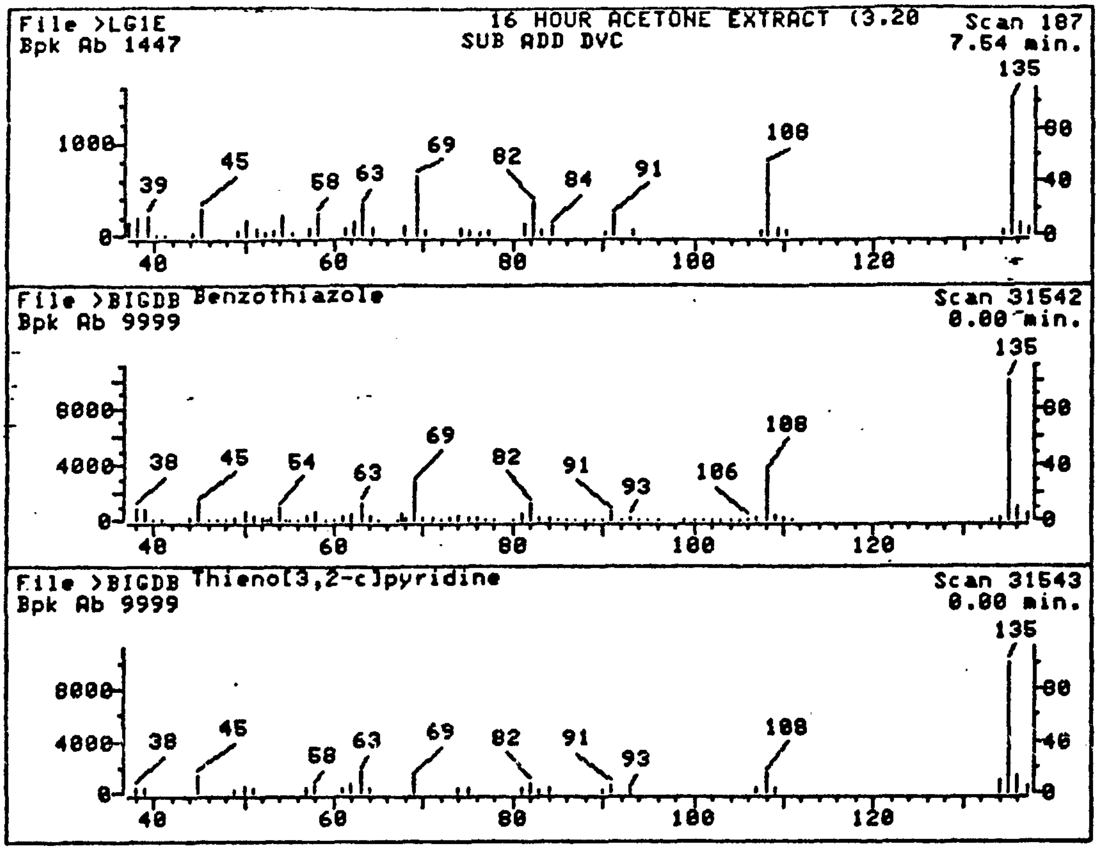
1. 4-Hydroxy-4-methyl pentanone
3. Decane
4. N-Isopropylidene-cyclohexylamine (Accelerator Decomposition)
5. Hydrocarbon
6. Benzothiazole (Accelerator Decomposition)
7. Hexadecanoic Acid
9. Octadecanoic Acid (Stearic Acid)
11. N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (Antioxidant)

Figure 7. The reconstructed mass chromatogram of the 16-hour acetone extract of Sample LG-1.



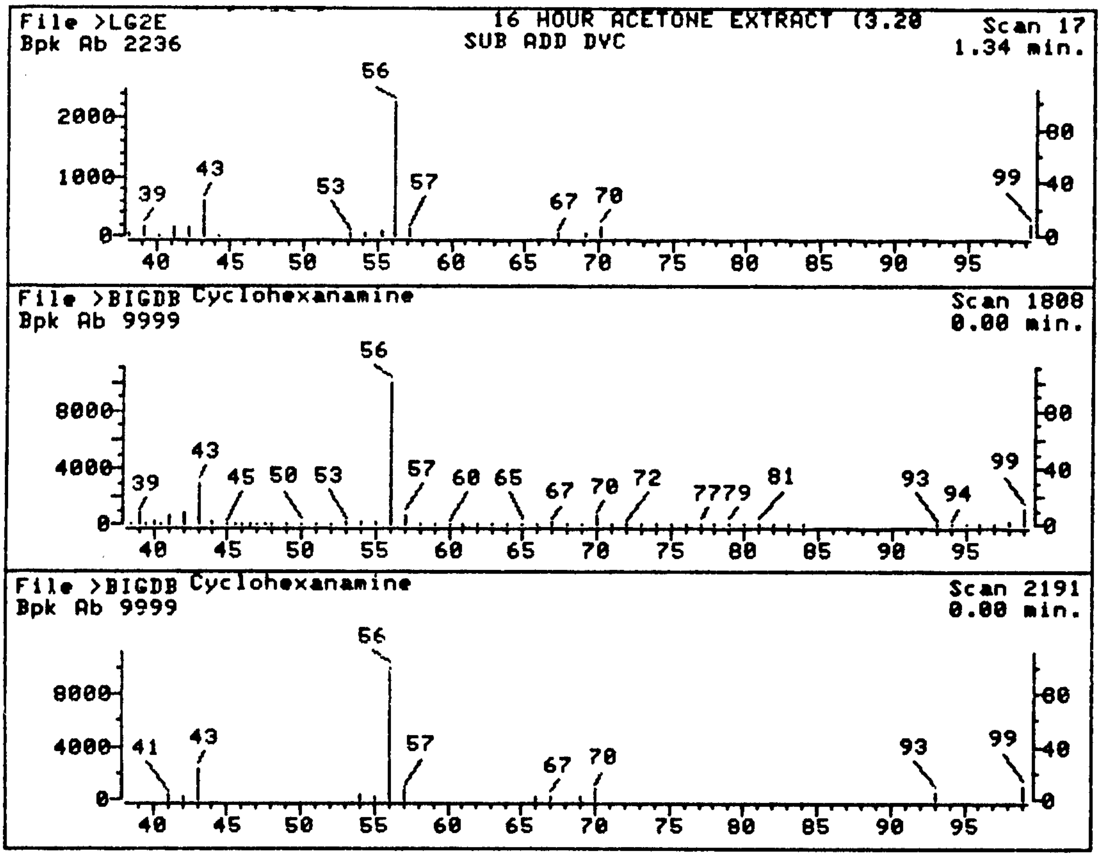
1. N-ISOPROPYLIDENE-CYCLOHEXYLAMINE 139 C9H17N
2. N-ISOPROPYLIDENE-CYCLOHEXYLAMINE 139 C9H17N
3. Azetidine, 1-cyclohexyl- 139 C9H17N
4. Cyclohexane, cyclopropyl- 124 C9H16
5. Spiro[3.4]octan-5-one 124 C8H12O

Figure 7a. The mass spectrum of N-isopropylidene-cyclohexylamine, m/z 139, found in Sample LG-1 (16-hour acetone extraction).



1. Benzothiazole — 135 C_7H_5NS
2. Thieno[3,2-c]pyridine — 135 C_7H_5NS
3. 1,2-Benzisothiazole — 135 C_7H_5NS
4. Benzothiazole — 135 C_7H_5NS
5. Benzothiazole — 135 C_7H_5NS

Figure 7b. The mass spectrum of benzothiazole, m/z 135, found in Sample LG-1 (16-hour acetone extraction).



COMPONENT IDENTIFICATION

1. 4-Hydroxy-4-Methylpentanone
2. Cyclohexanamine (Accelerator Decomposition)
3. 3-Methyl Pyrrolidine
4. N-Isoproplyidene cyclohexylamine (Accelerator Decomposition)
5. Hydrocarbon
6. N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (Antioxidant)
7. Hydrocarbon
8. Hydrocarbon

Figure 8. The reconstructed mass chromatogram of the 16-hour acetone extract of Sample LG-2.

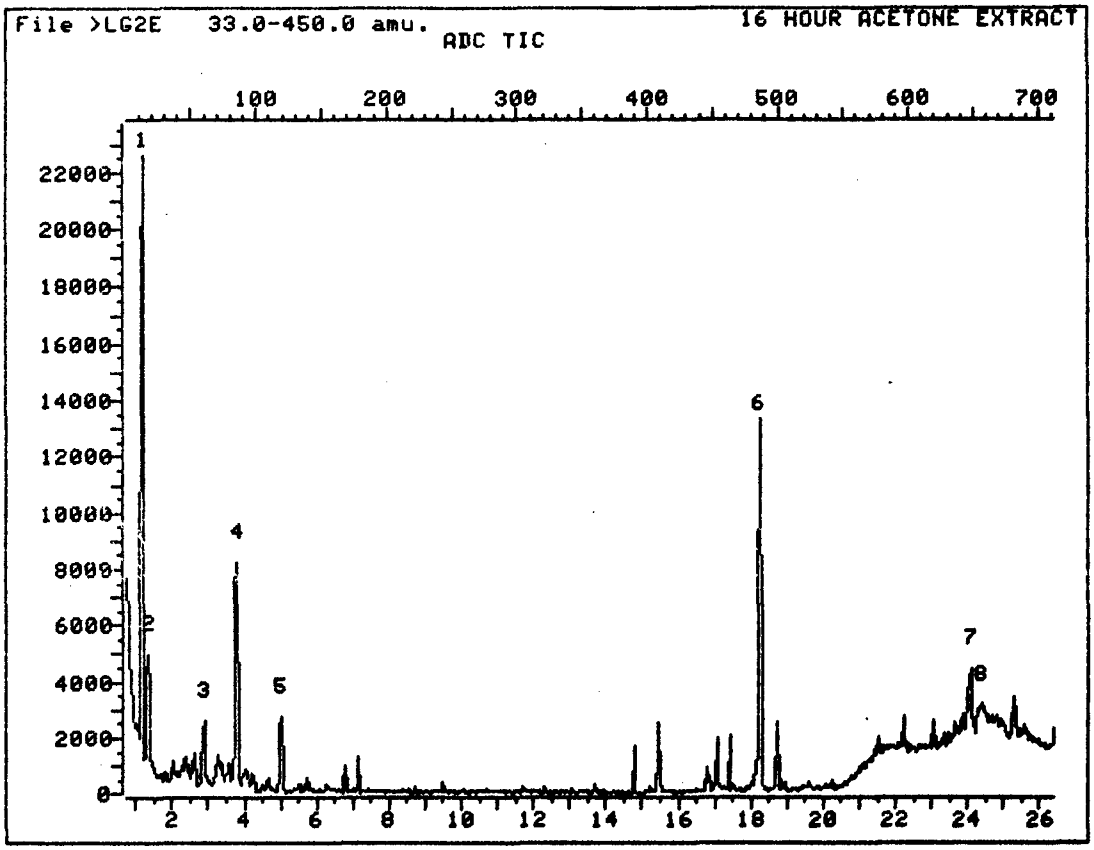


Figure 8a. The mass spectrum of cyclohexaneamine, m/z 99, found in Sample LG-2 (16-hour acetone extraction).

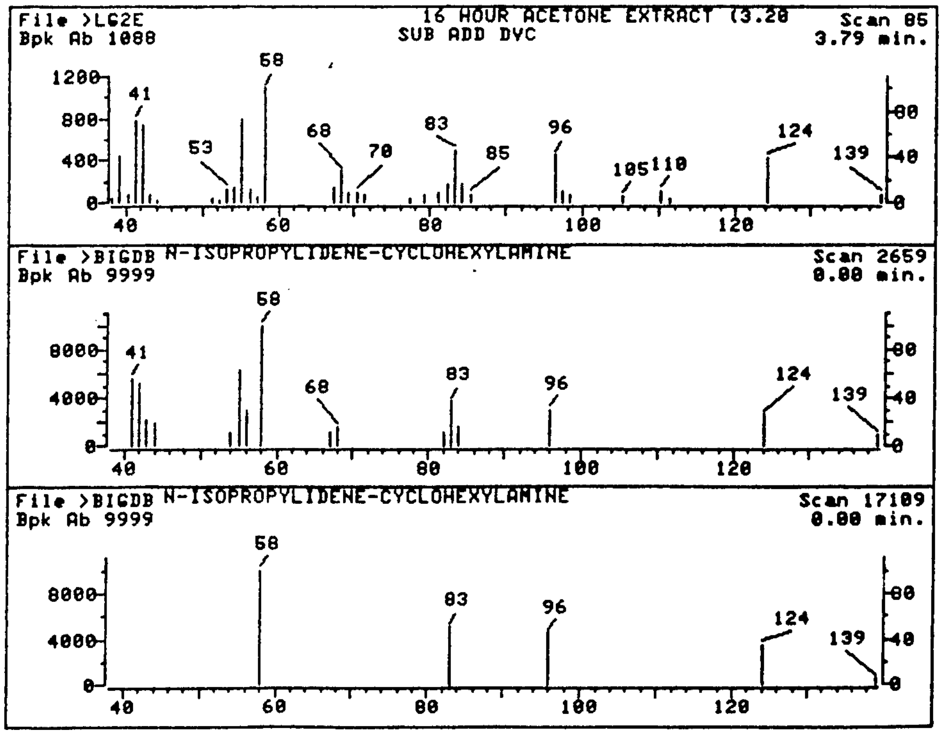


Figure 8b. The mass spectrum of N-isopropylidene-cyclohexylamine found in Sample LG-2 (16-hour acetone extraction).

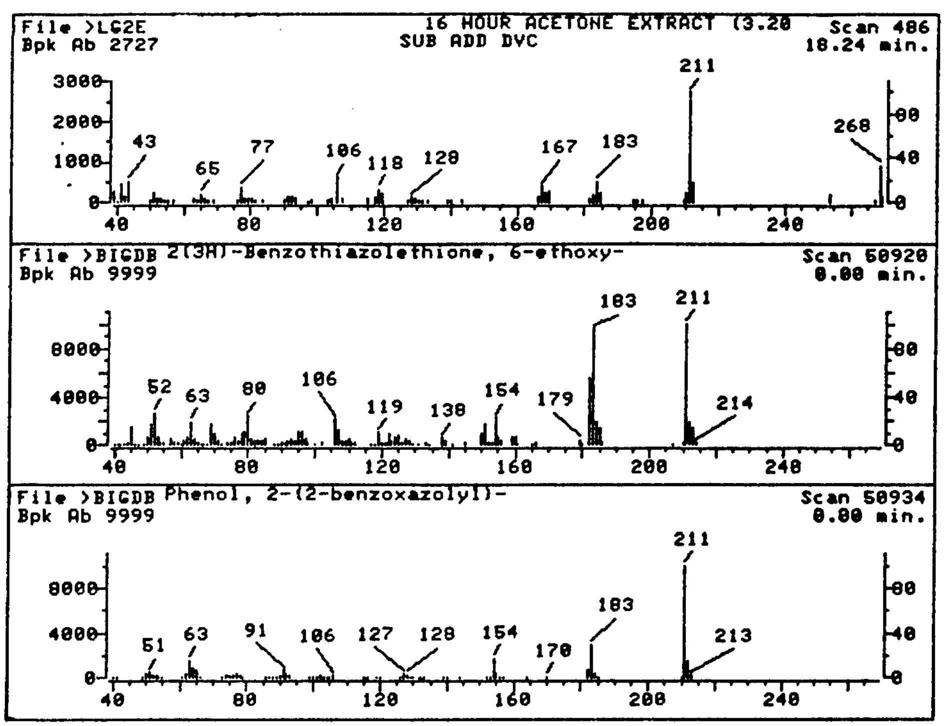


Figure 8c. The mass spectrum of the antioxidant [N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine], m/z 268, found in Sample LG-2 (16-hour acetone extraction).

DISTRIBUTION LIST

No. of Copies	To
1	Office of the Under Secretary of Defense for Research and Engineering, The Pentagon, Washington, DC 20301
	Commander, U.S. Army Laboratory Command, 2800 Powder Mill Road, Adelphi, MD 20783-1197
1	ATTN: Technical Library
2	Commander, Defense Technical Information Center, Cameron Station, Building 5, 5010 Duke Street, Alexandria, VA 22314
	Commander, Army Research Office, P.O. Box 12211, Research Triangle Park, NC 27709
1	ATTN: Information Processing Office
	Commander, U.S. Army Materiel Command, 5001 Eisenhower Avenue, Alexandria, VA 22333
1	ATTN: AMCLD
	Commander, U.S. Army Materiel Systems Analysis Activity, Aberdeen Proving Ground, MD 21005
1	ATTN: AMXSY-MP, H. Cohen
	Commander, U.S. Army Electronics Research and Development Command, Fort Monmouth, NJ 07703
1	ATTN: AMDSD-L
1	AMDSD-E
	Commander, U.S. Army Missile Command, Redstone Arsenal, AL 35898
1	ATTN: AMSMI-RKP, J. Wright, Bldg. 7574
4	AMSMI-TB, Redstone Scientific Information Center
1	AMSMI-RLM
1	Technical Library
	Commander, U.S. Army Armament, Munitions and Chemical Command, Dover, NJ 07801
2	ATTN: Technical Library
1	AMDAR-SCM, J. D. Corrie
1	AMDAR-QAC-E
1	AMDAR-LCA, Mr. Harry E. Pebly, Jr., PLASTEC, Director
	Commander, U.S. Army Natick Research and Development Center, Natick, MA 01760
1	ATTN: Technical Library
	Commander, U.S. Army Satellite Communications Agency, Fort Monmouth, NJ 07703
1	ATTN: Technical Document Center
	Commander, U.S. Army Tank-Automotive Command, Warren, MI 48090
1	ATTN: AMSTA-ZSK
2	AMSTA-UL, Technical Library
	Commander, White Sands Missile Range, NM 88002
1	ATTN: STEWS-WS-VT
	President, Airborne, Electronics and Special Warfare Board, Fort Bragg, NC 28307
1	ATTN: Library
	Director, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005
1	ATTN: AMDAR-TSB-S (STINFO)
	Commander, Dugway Proving Ground, Dugway, UT 84022
1	ATTN: Technical Library, Technical Information Division

No. of Copies	To
	Commander, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, MD 20783
1	ATTN: Technical Information Office
	Director, Benet Weapons Laboratory, LCWSL, USA AMCCOM, Watervliet, NY 12189
1	ATTN: AMSMC-LCB-TL
1	AMSMC-LCB-R
1	AMSMC-LCB-RM
1	AMSMC-LCB-RP
	Commander, U.S. Army Foreign Science and Technology Center, 220 7th Street, N.E., Charlottesville, VA 22901
1	ATTN: Military Tech, Mr. Marley
	Commander, U.S. Army Aeromedical Research Unit, P.O. Box 577, Fort Rucker, AL 36360
1	ATTN: Technical Library
	Director, Eustis Directorate, U.S. Army Air Mobility Research and Development Laboratory, Fort Eustis, VA 23604-5577
1	ATTN: Mr. J. Robinson, SAVDL-E-MOS (AVSCOM)
	U.S. Army Aviation Training Library, Fort Rucker, AL 36360
1	ATTN: Building 5906-5907
	Commander, U.S. Army Agency for Aviation Safety, Fort Rucker, AL 36362
1	ATTN: Technical Library
	Commander, USACDC Air Defense Agency, Fort Bliss, TX 79916
1	ATTN: Technical Library
	Commander, U.S. Army Engineer School, Fort Belvoir, VA 22060
1	ATTN: Library
	Commander, U.S. Army Engineer Waterways Experiment Station, P. O. Box 631, Vicksburg, MS 39180
1	ATTN: Research Center Library
	Technical Director, Human Engineering Laboratories, Aberdeen Proving Ground, MD 21005
1	ATTN: Technical Reports Office
	Commandant, U.S. Army Quartermaster School, Fort Lee, VA 23801
1	ATTN: Quartermaster School Library
	Naval Research Laboratory, Washington, DC 20375
1	ATTN: Dr. C. I. Chang - Code 5830
2	Dr. G. R. Yoder - Code 6384
	Commander, U.S. Army Radio Propagation Agency, Fort Bragg, NC 28307
1	ATTN: SCCR-2
	Chief of Naval Research, Arlington, VA 22217
1	ATTN: Code 471
	Commander, U.S. Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, OH 45433
1	ATTN: AFWAL/MLC
1	AFWAL/MLLP, M. Forney Jr.
1	AFWAL/MLBC, Mr. Stanley Schulman
	Director, U.S. Army Materials Technology Laboratory, Watertown, MA 02172-0001
2	ATTN: SLCMT-IML
3	Authors

U.S. Army Materials Technology Laboratory,
Watertown, Massachusetts 02172-0001
SERIAL CHROMATOPYROGRAPHY-MASS SPECTROMETRY OF NATURAL RUBBER VULCANIZATES - Alfred J. Deome, Christopher J. Kulig, and Jacob Patt

Technical Report MTL TR 86-4, March 1986, 15 pp - illus-tables, D/A Project 1L162601AH91

AD________________

UNCLASSIFIED
UNLIMITED DISTRIBUTION

Key Words

Gas chromatography
Mass spectrometry
Pyrolysis

Applications of serial pyrolysis-gas chromatography-mass spectrometry, developed at the U.S. Army Materials Technology Laboratory, are used to determine the qualitative organic formulation and polymer composition of two proprietary experimental natural rubber formulations.

U.S. Army Materials Technology Laboratory,
Watertown, Massachusetts 02172-0001
SERIAL CHROMATOPYROGRAPHY-MASS SPECTROMETRY OF NATURAL RUBBER VULCANIZATES - Alfred J. Deome, Christopher J. Kulig, and Jacob Patt

Technical Report MTL TR 86-4, March 1986, 15 pp - illus-tables, D/A Project 1L162601AH91

AD________________

UNCLASSIFIED
UNLIMITED DISTRIBUTION

Key Words

Gas chromatography
Mass spectrometry
Pyrolysis

Applications of serial pyrolysis-gas chromatography-mass spectrometry, developed at the U.S. Army Materials Technology Laboratory, are used to determine the qualitative organic formulation and polymer composition of two proprietary experimental natural rubber formulations.

U.S. Army Materials Technology Laboratory,
Watertown, Massachusetts 02172-0001
SERIAL CHROMATOPYROGRAPHY-MASS SPECTROMETRY OF NATURAL RUBBER VULCANIZATES - Alfred J. Deome, Christopher J. Kulig, and Jacob Patt

Technical Report MTL TR 86-4, March 1986, 15 pp - illus-tables, D/A Project 1L162601AH91

AD________________

UNCLASSIFIED
UNLIMITED DISTRIBUTION

Key Words

Gas chromatography
Mass spectrometry
Pyrolysis

Applications of serial pyrolysis-gas chromatography-mass spectrometry, developed at the U.S. Army Materials Technology Laboratory, are used to determine the qualitative organic formulation and polymer composition of two proprietary experimental natural rubber formulations.

U.S. Army Materials Technology Laboratory,
Watertown, Massachusetts 02172-0001
SERIAL CHROMATOPYROGRAPHY-MASS SPECTROMETRY OF NATURAL RUBBER VULCANIZATES - Alfred J. Deome, Christopher J. Kulig, and Jacob Patt

Technical Report MTL TR 86-4, March 1986, 15 pp - illus-tables, D/A Project 1L162601AH91

AD________________

UNCLASSIFIED
UNLIMITED DISTRIBUTION

Key Words

Gas chromatography
Mass spectrometry
Pyrolysis

Applications of serial pyrolysis-gas chromatography-mass spectrometry, developed at the U.S. Army Materials Technology Laboratory, are used to determine the qualitative organic formulation and polymer composition of two proprietary experimental natural rubber formulations.